

Computational Study of Electrochemical Windows of Room-Temperature Ionic Liquids

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Room-temperature ionic liquids (RTIL) are regarded as green solvents due to their low volatility, low flammability, and thermal stability. RTILs exhibit wide electrochemical windows, and they show potential as media for a variety of electroplating processes. Therefore, understanding the factors dominating the electrochemical stability of RTILs is crucial for improving the efficiency of separation processes. In this study, we computationally investigated the electrochemical properties of a series of imidazolium-based RTILs. The general trend of electrochemical windows of the RTILs studied is well reproduced, showing that it increases in the order of imidazolium < ammonium < pyrrolidinium < phosphonium giving confidence to the methodology presented to use it in screening studies of ionic liquids [1].

Room temperature ionic liquids (RTIL) are salts that are in molten states, typically below 100°C. Unlike common inorganic salts, which are composed of small-size ions, RTILs are comprised of bulky organic cations and ions. Due to their liquid state at room temperature, RTILs have found applications as solvents in various chemical and electrochemical processes. In comparison to conventional organic solvents, RTILs have the advantages of negligible vapor pressure, high thermal stability, low flammability, and tunability by fictionalizing the chemical structure of ions. Due to these advantages, they are considered

to be environmentally friendly solvents. Another notable property of RTILs is their intrinsic electrical conductivity, making them useful as solvents in electrochemical systems without the need for supporting electrolytes. In recent years, RTILs have been used in a variety of electrochemical processes such as lithium ion batteries, fuel cells, solar cells, and electro-depositions.

From the viewpoint of practical electrochemical operations, the electrochemical stability

of electrolytic media is one of the most important factors determining the utility and performance of electrochemical processes or devices. The electrochemical stability of the ionic liquid is characterized by the electrochemical window (ECW). The electrochemical window is defined as the potential interval between the cathodic and anodic potential

limits at which reduction and oxidation reactions of electrolytes occur at the electrodes. In this project, we aim to find reliable and efficient methods for modeling the electrochemical windows of the commonly used RTILs. With such methods, we hope, in future work, to screen for suitable candidate RTILs for certain electrochemical purposes among the huge number of RTILs developed so far, and to make predictions of the electrochemical properties for new RTIL systems.

We proposed four different approaches including gas phase method, polarizable continuum model (PCM), quantum mechanics/molecular mechanics (QM/MM), and thermodynamic cycle (TDC) method by running classical molecular dynamics (MD) simulations. These methods cover different degrees of approximation and computational cost from gas-phase calculations to full explicit solvation models. In the PCM model, as shown in Fig. 1(a), the solvent was treated as a continuous medium with the dielectric constant of the ionic liquid. An individual ion was embedded in solvents and a cavity was created, the surface of which was polarized to mimic the polarization of the solute species. For the QM/MM method, the reaction free energy changes were calculated using the two-layer ONIOM method of Morokuma and coworkers [2]. In this method, the reactive species are treated by first principle, while the environment is described by MM as illustrated by Fig. 1(b). The structures used for ONIOM calculations were taken from pre-equilibrated configurations with classical MD simulations. For the thermodynamic cycle method as depicted by Fig. 1(c), the calculation of free-energy change is reduced to two parts, the reaction free energy in the gas phase was calculated quantum mechanically, and the solvation free energy of the reactive species was estimated with thermodynamic integration. The modeling was based on the ionic liquid systems composed of imidazolium, ammonium, and phosphonium cations, and bistriflimide anions.

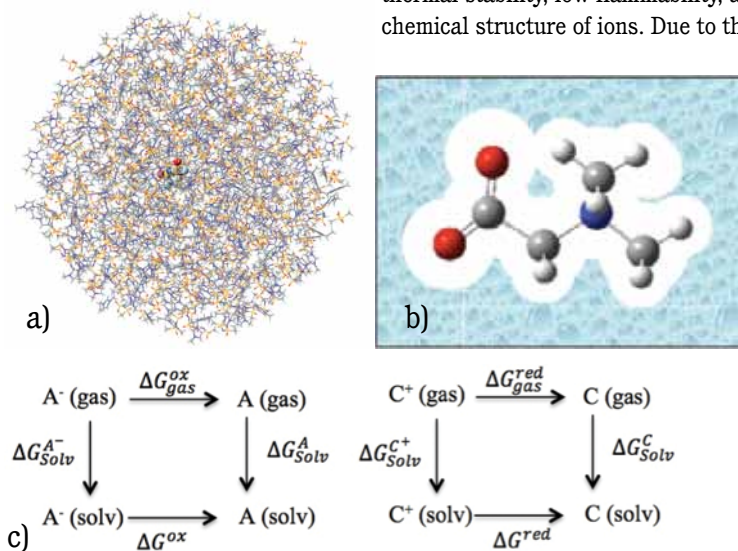


Fig. 1. Schematic diagram of the computational methods: (a) QM/MM; (b) PCM; (c) thermodynamic cycles (TDC).

As shown in Table 1, the calculated windows via the gas phase method are far from experimental values. However, the calculated windows via the isolated-ion method PCM, QM/MM, and TDC methods predict consistent results that agree fairly well with experiment for the ionic system of [C₂MIM][Tf₂N]. Therefore, solvation effect plays an important role in determining RTIL electrochemical windows. We found that to predict the electrochemical windows of RTILs, the PCM model represents a reasonable compromise between accuracy and efficiency. Figure 2 shows the PCM calculated electrochemical windows against the experimental values for a set of RTILs. The general trend reproduced well, showing that the windows increase in the order of imidazolium < ammonium < pyrrolidinium < phosphonium.

Table 1. The calculated potentials and electrochemical windows (in V) of [C₂MIM⁺][Tf₂N⁻]

	V_{ox}	V_{red}	ECW	Exp.
<i>vacuo</i>	5.40	-4.56	0.84	4.1
PCM	7.00	-2.72	4.28	4.5
TDC	7.02	-2.55	4.47	
ONIOM	7.55	-2.94	4.61	

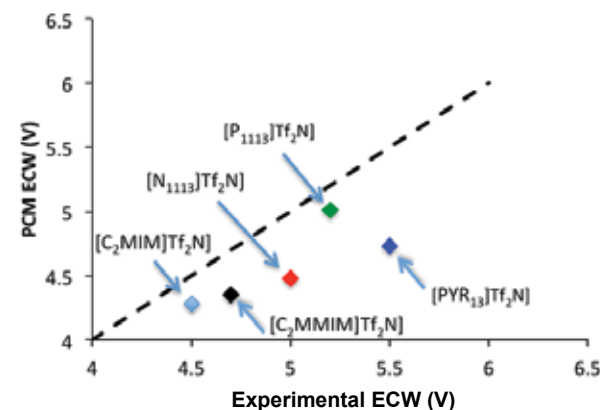


Fig. 2. The plot of experimental ECW against the PCM calculations.

[1] Tian, Y.-H. et al., *J Phys Chem B* **116**, 11943 (2012).

[2] Dapprich, S. et al., *J Molecular Structure: THEOCHEM*, **1**, 461 (1999).